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TRANSLATION:

DISTRIBUTION OF VARIOUS TOBACCO SMOKE COMPONENTS IN MAINSTREAM AND SIDESTREAM SMOKE

A Review*

by

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(9) Ammonia, Amines, Nitrogen Bases

(10) Nitrogen Oxides

(11) *N*-Nitrosamines

(12) Hydrocarbons

(13) Gas-Phase Components

(14) Phenols

(15) Polycyclic Hydrocarbons and Aza-Polycyclic Compounds

(16) Steroids

(17) Heavy Metals

IV. Concluding Remarks

"The actual account of the substance and the mainstream to sidestream ratio will vary with different types of tobacco tested and the method used to burn the cigarette ..... Many of the substances, including nicotine, carbonmonoxide and ammoniac are found in much higher concentrations in the sidestream smoke than in the mainstream smoke. Thus, the total smoke exposure of nonsmokers is quantitatively much smaller than the exposure of smokers, but the smoke nonsmokers inhale may be quantitatively richer in certain compounds than mainstream smoke. This qualitative difference in smoke exposure makes the quantification of the involuntary smoking in terms of "cigarette equivalents" confusing and inaccurate. It requires that involuntary smoking be evaluated as a separate problem not subject to simple extrapolation of an understanding of dose-response relationship of cigarette smoking."

I. INTRODUCTION

Sidestream smoke is especially important with regard to the health risks discussed in connection with the use of tobacco. The reason is obvious: If tobacco smoke represents a risk factor to the active smoker, it is possible that this factor could also exist in a milder form for the nonsmokers present in smoky rooms. If proof could be presented that this is in fact the case, the demand for legal protection for non-smokers from the dangers of tobacco smoke would be justified. On the basis of the relevant literature, which is still relatively easy to encompass, a survey is to be given here of the methods described up to now for measuring the sidestream smoke of cigarettes and cigars and for determining its composition in comparison with that of mainstream smoke.

According to the Coresta definition, mainstream smoke (MS) is the smoke which leaves the cigarette, cigar, or pipe while the smoker is drawing in at the mouth end and which reaches the organism of the smoker directly [21]. The smoke which is given off to the surroundings during smoking pauses, however, is called the sidestream smoke (SS). According to Lipp, this consists of the fire stream, the diffusion stream, and the glow stream [76]. These relationships are illustrated schematically in Figure 1 to clarify them.

Figure 1.

It is obvious that diffusion stream and fire stream smoke also escape during the puff into the surrounding room air, but in terms of quantity these components can be ignored.

The tobacco smoke aerosol is formed by complex interactions of distillation and sublimation processes and by pyrolysis, pyrosynthesis, and combustion

processes. Determining for the qualitative and quantitative composition of this aerosol are not only the tobacco material present in the cigarette and its pretreatment and the porosity and quality of the cigarette paper used, but also the type and performance of the filter, if present*, and especially the temperature which prevails in the burning tip [13]. During a puff this temperature is around 900°C, and in the pauses between puffs it decreases by more than 300°C to less than 600°C. This is therefore the necessary precondition for the existence of qualitative and quantitative differences in the composition of mainstream and sidestream smoke.

The first indications that such differences actually do exist date back to an article by Wenusch published in 1930 [136]. He found that the mainstream and sidestream smoke from Oriental tobacco cigarettes differ in pH, i.e., the mainstream smoke had a weakly acidic reaction, the sidestream smoke a weakly alkaline one. Even at that early date he was able to show that this is the result of differences in combustion. During the pauses between puffs, he blew a stream of air onto the glowing tip of the cigarette and found that the pH of the escaping sidestream smoke fell and approached that of the mainstream smoke.

Inquiries into the mechanism of smoke formation in a cigarette were made in 1963 by Egerton et al. [28] and by Baker and Kilburn [2]. These studies are summarized in the articles by Johnson [60] and Baker [4]. The data to be found in these studies should also be given here for the sake of completeness.

According to Egerton [28], the boundary zones of the glowing cone of the cigarette burn much more rapidly during a puff than the central part. A

*The articles by Gori [32], Hecht et al. [39], Hoffmann and Wunder [42], Keith [64], Kensler [66], Lus and Kuhn [68], Kuhn and Klus [73], Tigglebeck [129], Tso et al. [130], and Weber [133] show how, for example, the composition of the mainstream smoke can be affected. This list does not claim to be exhaustive.

temperature increase during the puff is observed primarily in the peripheral region. In contrast, during pauses between puffs the center of the glowing cone smolders more rapidly than the marginal zones.

During the puff, the compounds forming in the hot outer boundary layer are drawn into the cigarette, whereas the gas layer around the tip of the glowing cone itself remains almost unchanged. This is also true for the axial regions of the glowing cone.

Jenkins et al. [51] were able to show by means of radioactively-labeled tracer substances which had been introduced into the center or the boundary zone of cigarettes that the particle phase of mainstream smoke is formed essentially at the periphery of the cigarette, the same being true for the components of the particle phase of sidestream smoke which are formed by thermal decomposition of nonvolatile substances. The gas phase of the sidestream smoke and the portion of its particle phase in which volatile and sublimable substances of the cigarette participate are formed primarily in the central, internal part. By way of the thermal decomposition of nonvolatile substances, the external zone of the cigarette again plays a role in the formation of the gas phase of mainstream smoke.

The component of the mainstream smoke gas phase which forms from the volatile and sublimable compounds of the tobacco is not bound to a specific region of the glowing cone. During pauses between puffs, these compounds decompose under the effect of temperature or are oxidized. The gaseous products forming here are transferred at the beginning of the puff into the mainstream smoke by the air entering the cigarette. Kilburn [67] proposed this mechanism in association with the formation of carbon monoxide.

Baker pointed out that the quantitative ratio of an individual compound in the mainstream and sidestream smoke depends on the specific mechanism of its formation. [4].

It must be remembered, however, that about four times as much tobacco burns during the pause between puffs as during the puffs [55].

The distribution of several compounds treated in this review article in the mainstream and sidestream smoke reflects this quantitative ratio.

Initial studies of sidestream smoke with regard to its content of total condensate, nicotine, pyridine bases, and ammonia are found in Pyriki [102-106], Wenusch [137], Preiss [101], and Müller and Moldenhauer [80]. In their studies, however, the researchers were not able to carry out large numbers of experiments [83] or to produce accurate, comparable data on the occurrence and distribution of various smoke contents in mainstream and sidestream smoke because of the nature of the experimental equipment used, the smoking parameters employed, and the chemical-analytical methods available. The "smoking cartridge" developed by Neurath et al. made it possible for the first time to measure sidestream smoke quantitatively [82, 83]. This device was used in modified form especially by Hoffmann's group (Naylor Dana Institute for Disease Prevention, Valhalla, New York, U.S.A.) for their studies [9].

II. METHODS FOR MEASURING SIDESTREAM SMOKE

The apparatus used by Hoffmann's group for the study of sdiestream smoke [9] is shown schematically in Figure 2. As already mentioned, this chamber represents a modification of the device proposed by Neurath [82]. Most of the currently available quantitative data on the composition of sidestream smoke have been obtained with this apparatus.

Figure 2.

Sidestream smoke is rinsed from the chamber by means of a continuous stream of air. Neurath rinses with 20-25 ml [83], Brunnemann with 25 ml per second [9]. The heat released as the cigarette burns can be removed by means of a water cooling system. At this point it should be emphasized that the smoking of a cigarette in this sidestream smoke chamber is in no way comparable with the analytical smoking according to ISO 3,308 [49] or DIN 10,240, Part 1 [26]. In the uncooled chamber, temperatures of 30-64°C were measured 8 mm in front of the burning end of the cigarette, these temperatures being dependent on the number of puffs and on the number of cigarettes smoked in succession [69]. A temperature of more than 90°C was even measured in the sidestream smoke outlet. The measurement values were only slightly lower in a chamber which was temperature-controlled by means of 20°C-water. The temperature curves are given in Figures 3 and 4.

Figure 3.

Figure 4.

The humidity in the chamber is 100% because of the water forming during combustion; this water condenses on the cold glass walls. It is not impossible under these conditions that the composition of mainstream and sidestream smoke will differ from that determined during analytical smoking in the standard climate (20-22°C, 60-65% relative humidity). The mainstream amoke values of commercial cigarettes which were obtained with and without the modified Neurath chamber can serve as an example; these values are summarized in Table 1 [70].

Table 1.

According to the results shown in the table, the wet condensate value obtained during smoking in the chamber is up to 35% higher than that obtained without the effect of the chamber. In the dry condensate, this difference is up to 21%.

We cannot give any explanation as to why the difference is not constant for the various types of cigarettes tested. The cigarettes for this study were smoked by means of a single-channel machine from Borgwald; the condensate was precipitated on Cambridge filters. These results confirm the results found in another industrial laboratory, where for the dry condensate under the effect of the modified Neurath chamber an increase in the values of around 20% was found [29].

Aside from this criticism, however, the values found by means of the modified Neurath chamber are on the same order of magnitude for certain components as those determined during burning in the open. Jermini et al. [53], for example, found about 1 ppm NO in the room air after 15 cigarettes were smoked in a 30-m^3 room. This corresponds to an NO emission of the sidestream smoke of 2.7 mg per cigarette. Adams et al. determined the NO content in the sidestream smoke with the help of the modified Neurath chamber and found 2-3 mg per cigarette [1]. In summary it can be said that the values obtained with this sidestream smoke chamber must be taken with certain reservations.

Another possibility for collecting sidestream smoke has been proposed by Johnson et al. [55]. A similar arrangement was used by Browne, Keith, and Allen for their studies [8]. As can be seen in Figure 5, the burning cigarette is located perpendicularly to the longitudinal axis of a cylinder; overheating and excess humidity in the smoke chamber are not to be expected, but unfortunately no exact data are available.

Figure 5.

At the 32nd Tobacco Chemists Research Conference in 1978, Harris and Hayens presented an additional possibility for measuring sidestream smoke [37]. In a 20-channel smoking machine with a rotating smoking head, small exhaust hoods are mounted over the glowing cones of the cigarettes to collect the sidestream smoke, whereby only the burning ends of the individual cigarettes are covered. The collected smoke/air stream is conducted to a suitable precipitation system. . . . [Beginning of sentence cut off at top of page -- *Tr. Ed.*] on a Cambridge filter is strongly dependent on the chosen flow rate. At a flow rate of 35 ℓ/min, only 23% of the supplied nicotine is retained on the filter, but 99% is retained at an air flow of 1 liter per minute.

No direct comparison of this sidestream smoke apparatus with the devices used by other research groups has yet been made. On the basis of the data given by Harris and Hayens for the distribution of various smoke components in the mainstream and sidestream smoke, however, it can be seen that the results obtained with this device generally correspond to those obtained with the units already described.

In his study on harmane and norharmane in cigarette smoke, Neurath collected the sidestream smoke by means of a funnel 120 mm in diameter with a lateral notch for the cigarette [88]. The smoke was conducted across a Cambridge filter with a diameter of 44 mm by an air stream of four liters per minute in order to precipitate the components. Yoshida also uses a similar apparatus to test fresh sidestream smoke. In order to avoid as far as possible any influence on the smoking of the tested cigarette exerted by changes in temperature and relative humidity, Jermini et al. smoked the cigarettes in a 30-m^3 climate-controlled

chamber or in a 272-ℓ Plexiglass box [53]. On the basis of air samples in which the content of various tobacco smoke components was determined, conclusions could be drawn as to the amount occurring sidestream smoke. Brunnemann, Fink, and Moser chose a similar experimental set-up for the determination of volatile nitrosamines in sidestream smoke [17]. The nitrosamine content of the sidestream smoke was also determined by Hoffmann's group, which made use of a 400 ℓ Clove box, among other methods.

Yoshida et al. studied the effect of filter ventilation, paper porosity, and tobacco fill weight of cigarettes on the carbon monoxide content of the mainstream and sidestream smoke by means of a Clove box also, this one with a capacity of 150 ℓ [142].

When a Clove box or a closed experimental space is used to test sidestream smoke, however, it must be remembered that the smoke is subject to aging effects. In addition to a physical change, there is also a change in the quantitative chemical composition of the smoke associated with this aging.

The sedimentation of the smoke aerosol is also to be considered. Specifically, this topic will be discussed in the following chapter. It is therefore necessary to exercise extreme caution when drawing conclusions as to the fresh sidestream smoke from findings which are obtained by means of an experimental volume of this type or a Clove box, whereby the position of the chamber at which the air sample is withdrawn also has an effect on the measurement value. Even the transfer of the results obtained with a chamber of this type to larger volumes can also lead to erroneous estimates for the same reasons.

III. DISTRIBUTION OF VARIOUS TOBACCO SMOKE COMPONENTS IN MAINSTREAM AND SIDESTREAM SMOKE

1. Nicotine and Other Tobacco Alkaloids

As early as 50 years ago, the first data on the distribution of this alkaloid with respect to the two smoke streams were published as part of the effort to set up a nicotine balance for cigarettes [80, 101, 102, 103, 104, 105, 106, 137, 139]. The results found at that time, however, are comparable to only a certain extent with those found with modern cigarettes because of the experimental set-up chosen, the smoking parameters, and finally the nature of the tested cigarettes.

It was only in 1964 that Neurath et al. presented the nicotine balance of a nonfilter, 80-mm, blended cigarette; for this the cigarette was smoked according to the conditions which were later established in the relevant German Industrial Standards (DIN) and in the ISO regulations [83] (conditioning at 65% relative humidity and 20°C; one puff per minute; two-second puff length; 35 ml puff volume; 23-mm butt length). The sidestream smoke was measured by means of the Neurath chamber. According to these authors, 10.5% of the nicotine present in the tobacco passes into the mainstream smoke (MS) and 28.2% into the sidestream smoke. The ratio of SS to MS is therefore 2.7.

Johnson et al. tested the nicotine content of the two smoke streams from 85-mm nonfilter cigarettes from Burley, Virginia, and Oriental tobaccos. In addition, the Kentucky Reference Cigarette 1R1 was included in the study [55]. The sidestream smoke was collected by the device proposed by this group. The ratios found for sidestream smoke to mainstream smoke are given in Table 2.

Table 2.

For a nonfilter U.S.-blend cigarette, Brunnemann also finds a ratio of 2.7 [12]. Browne et al. provide data on the nictoine content of filter cigarettes with and without filter ventilation [8]. As can be seen from the following table (Table 3), the nicotine content of the sidestream smoke increases with increasing ventilation.

Table 3.

It is of interest that according to this study, the nicotine in the mainstream smoke is present almost completely in the form of the salt in the particle phase. In the sidestream smoke, however, most of it is in the gas phase, whereby the ratio shifts with increasing degree of ventilation in the favor of the solid-liquid phase. The reason for the increased level of gas-phase nicotine in the sidestream smoke is the alkaline smoke pH, which leads to the fact that most of this alkaloid is present in nonprotonated form as a free base. The nicotine determination in the sidestream smoke was carried out by the authors by means of UV spectrophotometry after steam distillation. With this process, pyridine and its alkyl derivatives in addition to some of the pyrazines of the tobacco smoke are also included. According to Brunnemann, Stahnke, and Hoffmann, 1.8 mg of these compounds are found in the sidestream smoke of an 85-mm nonfilter, U.S.-blend cigarette [16]. It is therefore possible that the nicotine value is falsified, but the chosen condensate precipitation system plays a role here as well.

The importance of the condensate precipitation system in the measurement of nicotine in sidestream smoke can also be seen from the study by Yoshida [141]. He used cigarettes of Burley-21, Bright-Yellow, and Matsukawa tobacco for his studies in addition to a commercial cigarette. Both the mainstream and the

sidestream smoke were conducted across Cambridge filters and then through a liquid trap filled with 0.1 *N* hydrochloric acid. The smoke nicotine was determined by gas chromatography (10 Carbowax 20 M on Chromosorb AW). The sidestream smoke was collected by means of a funnel (diameter, 7 cm) located over the burning end of the cigarette, through which the smoke was drawn off by a stream of air at the rate of eight liters per minute. Whereas in all cases practically 99.9% of the supplied nicotine remained on the Cambridge filter in the case of the mainstream smoke, the value ranged between 28.6% (Burley-21) and 48.9% (commercial cigarette) for the sidestream smoke depending on the type of tobacco. For the distribution between sidestream and mainstream smoke, values between 2.39 and 3.04 are given. They are thus on the same order of magnitude as those of the other authors.

Yoshida also tested the nicotine content in the air of a 10-m^3 room after the smoking of cigarettes. The air was again drawn through a trap system at a rate of eight liters per minute (sampling time, 60 mins). It is of interest that Yoshida could find only 1/900 of the sidestream nicotine emitted by the smoked cigarettes in the room air, whereby on average 89.4% of the alkaloid present could not be precipitated on the Cambridge filter upstream from the liquid.

Yoshida's findings are in our opinion a clear indication of the problems involved in transferring the measurement data obtained with defined collection devices for fresh sidestream smoke to the content in the air of specific components of tobacco smoke in larger volumes. This problem is caused by the dynamics of the coagulation and sedimentation of the smoke particles and by the chemical changes caused by aging. This is also true, of course, for the reverse logic.

In the case of cigarettes whose nicotine was labeled with ^{14}C, SS/MS ratios for the radioactivity (nicotine and its pyrolysis products) in the range of 2.94--4.11 were found [47, 50, 74, 115, 128]. For nicotine, Houseman found the ratio

of 2.78 by gas chromatography [47]. It is remarkable that this author, who carried out his experiments with 70-mm English cigarettes, found no nicotine in the gas phase of the sidestream smoke, in which he was able to detect, however, 21% of the ^{14}C activity used.

Schmeltz et al. also established by means of ^{14}C-labeled nicotine (random-labeled) that for a U.S.-blend cigarette, 16% of the supplied tobacco nicotine passes undecomposed into the mainstream smoke and 24% into the sidestream smoke [115].

Müller provides data on the effect of paper porosity on the nicotine content of the sidestream smoke of nonfilter and filter cigarettes [81]. In nonfilter cigarettes, the increase in porosity from 8 to 52 $ml/cm^2 \cdot min$ leads to 29.2% more nicotine in the sidestream smoke, but to a decrease in the mainstream smoke by 14.6%. The corresponding figures for filter cigarettes are +13.8% and −9.2%.

According to Neurath, tobacco moisture affects the composition of the mainstream and sidestream smoke decisively [84]. The values for nicotine are given in Table 4 as obtained for the smoking of a nonfilter 80-mm strand cigarette.

Table 4.

As the level of tobacco moisture increases, therefore, there is a shift in the nicotine content in favor of the sidestream smoke. For all of Neurath's data, however, the same reservations apply as to those for the data published by Browne [8], because here, too, the nicotine values were obtained by UV spectrophotometry. As a footnote to the table, it can be said that cigarettes are normally offered for sale to the consumer with a tobacco moisture of around 10.5%.

Additional data on the nicotine distribution between mainstream and sidestream smoke can be found in Harris and Hayens [37]. For nonfilter cigarettes,

they give a SS/MS ratio of 3.3-6.1, for filter cigarettes a ratio of 18-28. The tested filter cigarettes were equipped with ventilated high-performance filters in some cases. This explains why some of the ratios given by these authors are much greater than those published by other research teams.

Cornell, Cartwright, and Olender [22] describe the distribution of nicotine between the mainstream and sidestream smoke of cigars. Average-sized cigars with an average weight of 2.7 g were tested. They were smoked under the standard conditions established for cigarettes (1 puff per minute, 35 ml puff volume, 2-second puff length). The SS/MS nicotine ratio was between 5.5 and 12.0. Nicotine is therefore somewhat more concentrated in the sidestream smoke of cigars than in that of nonfilter cigarettes.

Except for one publication, nothing has been published on the occurrence of subsidiary tobacco alkaloids in the relevant literature.

In their study on the pyrolysis products of nicotine in model experiments and during the smoking of cigarettes, Schmetlz et al. also determined the myosmine and bipyridyl concentrations formed from ^{14}C-labeled nicotine [115].

With the use of a random marking system, they found for myosmine no activity in the mainstream smoke, but 0.7% of the original activity in the sidestream smoke. For 3,2'-bipyridyl, they found 0.1% in the mainstream and 0.2% in the sidestream. The experiment was carried out with 85-mm nonfilter U.S.-blend cigarettes, into which the labeled nicotine was injected by means of a syringe.

2. Dry Condensate

Neurath, in his studies of sidestream smoke, finds 52.0 mg of dry condensate per cigarette and 31.4 mg in the mainstream smoke [83]. The ratio is therefore 1.66. According to Wynder and Hoffmann, the condensate content of the sidestream smoke is 50-150% higher than that of the mainstream smoke [140].

Brunnemann gives the SS/MS condensate ratio in the smoke streams of an 85-mm, nonfilter U.S. cigarette as 1.7 [12].

Data for the condensate values of the sidestream smoke from filter-ventilated cigarettes can be found in Browne and in Table 5 [8].

Table 5.

As the filter ventilation increases, so does the SS/MS quotient. The values for the unventilated cigarette and the 33%-ventilated cigarette contradict the data of other authors, who found a higher condensate content in the sidestream than in the mainstream smoke. No explanation for this is suggested by Browne. The reason is possibly the different methods used to collect the sidestream smoke. Another reason could be that the condensate component of the mainstream smoke retained by the filter is included as part of the mainstream smoke. The other authors do not consider this component retained by a 23-mm tobacco butt or filter in their data.

The effect of tobacco moisture on the dry condensate content of the sidestream smoke of nonfilter German-blend cigarettes is discussed by Neurath [84] (Table 6).

Table 6.

Whereas the condensate content of the mainstream smoke remains the same as the moisture content increases, or decreases slightly, the sidestream smoke condensate definitely decreases. According to Neurath, this is caused by the decrease in the amount of burning tobacco as the moisture increases during the pauses between puffs. When the dry sidestream smoke condensate is considered

as a function of the amount of burned tobacco, the slightly concave curve shown in Figure 6 is obtained.

Figure 6.

According to Keith, there are $1.05 \cdot 10^{12}$ particles in the mainstream smoke of a cigarette and $3.5 \cdot 10^{12}$ particles in the sidestream smoke [63]. A SS/MS ratio of 3.3 results.

Hoegg studied the amount of condensate emitted by the sidestream smoke in a 25^3-m air-tight chamber and compared it with that of the mainstream smoke [40]. The nonfilter Kentucky Reference Cigarette 1R1 was used as the test cigarette. Up to 24 cigarettes were smoked by machine for the measurement. Because of the experimental set-up chosen (macrochamber), the effect of the burning of the cigarette as affected by excessive temperature and humidity, as can occur in the collection units used by other authors for sidestream smoke, is largely avoided. Hoegg finds 36.2 mg of total condensate per cigarette for the mainstream smoke and 25.8 mg for the sidestream smoke, and a SS/MS ratio of 0.7*. The author indicates in his article that the amount of condensate caused by the sidestream smoke decreases logarithmically by virtue of coagulation and sedimentation (Figure 7). This decrease can be described by the equation:

*The SS/MS ratio found by Hoegg corresponds to that given by Browne [8], but does not agree with the data of other authors [12, 83, 140]. In contrast to the other authors, Browne assigned the condensate component retained by the filter or butt to the mainstream smoke. We cannot say whether this is also the case for the data published by Hoegg. It is also possible that the smoke chamber itself also plays a role. In contrast to Hoegg and Browne, the other authors [12, 83, 140] used the Neurath chamber, or in some cases a modified Neurath chamber.

where Z = the number of cigarettes smoked; V = the size of the room in m^3; t = = the time in minutes after the cigarettes were lit; and TPM = the total condensate in the room air.

Figure 7.

The particle size of the sidestream smoke particles and their distribution has been described by Keith and Derrick [63]. According to these authors, the average particle size in fresh sidestream smoke is 0.15 µm with a lower limit of 0.08 µm. $6.3 \cdot 10^9$ particles are released per second in the sidestream smoke. On the basis of the coagulation rate of the mainstream smoke particles, the authors conclude that the average particle size in the sidestream smoke increases to 0.3 µm without four minutes. The size range of the particles is shifted within four minutes to 0.7 µm in the direction of larger smoke particles. The coagulation rate is further increased by the movement of the air -- e.g., in closed rooms. The average particle size in unaged mainstream smoke according to Keith and Derrick is 0.20-0.23 µm. This therefore results in a SS/MS ratio of 0.68.

Hoegg also studied the particle size in the sidestream smoke [40]. He found that most of the particles are less than 0.7 µm. Over an observation period of three hours, no particles larger than 2 µm were found.

McCusker et al. determined the aerodynamic mass median of the diameter for cigarettes and cigars low in smoke condensate [24, 25]. The values found by this group for the mainstream smoke of the cigarettes are between 0.52 and 0.67 µm, while the values for the sidestream smoke are between 0.47 and 0.54 µm. For the cigar smoke, 0.46 µm (SS) and 0.40 µm (MS) were found. The determinations were made four seconds after the smoke formed. The values for the mainstream smoke are definitely higher than those found by Keith in a more recent study [65].

For the mass median diameter of filter-ventilated cigarettes as a function of paper quality and the degree of filter ventilation, Keith found values between 0.325 and 0.354 µm (MS, fourth puff). According to Keith, the particle size increases very rapidly during the aging of the smoke by coagulation. Within one second, the mass median diameter doubles. The author points out, therefore, that the particle size determination must be carried out within 0.05 second after the smoke has formed, whereby here, too, the particles have increased in size already by 0.03-0.04 µm. This explains the higher values found by McCusker et al. Okada et al. also studied the size distribution of the aerosol particles in the mainstream and sidestream smoke by means of light scattering [89]. For the mainstream smoke particles they give an average geometric radius of 0.18 µm with a logarithmic standard deviation of 0.4; for the sidestream smoke particles they give 0.10 µm with a logarithmic standard deviation of 0.4. According to Baker [4], the difference in sizes between the mainstream and sidestream smoke streams reflects the different cooling rates and the extent of air admixture to which the vapors of the starting materials are subjected.

The same research team studied the effect of relative humidity on the growth of the particles in mainstream and sidestream smoke [48]. For this study, non-filter, 70-mm blend cigarettes were used, and the determination was made by light scattering. The particle size increases by less than 10% both in the mainstream smoke and in the sidestream smoke at a relative humidity of less than 90%. For the mainstream smoke, an average geometric radius of 0.110 µm was found at a relative humidity of 45%; at 55% the value was still 0.110 µm; at 64%, the value was 0.113 µm; and at 75%, a value of 0.115 µm was found. The values for fresh sidestream smoke were:

-- 16% relative humidity: 0.081 µm,

-- 51% relative humidity: 0.080 µm,

-- 73% relative humidity: 0.083 µm,

-- 84% relative humidity: 0.085 µm,

-- 94% relative humidity: 0.088 µm.

By way of equations derived from the measurement data, the authors show that the radius of the smoke particles doubles at a relative humidity of 99.5% and that there is no difference between the behavior of the mainstream and that of the sidestream smoke.

The change in the particle size distribution of the sidestream smoke over time is important in connection with involuntary smoking, because as the particle size increases, the inhalability of the particles decreases.

In a recently published study, Jenkins et al. studied the distribution of the carbon of the individual tobacco types contained in the Kentucky 1R1 Reference Cigarette between the two smoke phases [52]. In addition to the individual tobacco types, the paper required for the production of this cigarette, the moisture-retaining agent glycerol, and the added invert sugar were also included in the study. The various individual components were uniformly labeled with ^{14}C. As can be seen from Table 7, the actual contribution of the carbon of the cigarette components to the individual smoke phases differs in some cases quite a bit from the theoretically calculated amounts.

Table 7.

The Virginia leaf material introduces more carbon than calculated into the particle phase of the mainstream smoke; in the case of the Virginia ribs, the opposite is the case. The contribution of the Burley tobacco to the carbon in the mainstream smoke particle phase is only 77% of the calculated value, whereas

that of the Oriental component is 121%. Glycerol supplies 218% more carbon than calculated, and paper provides the theoretical value. The high carbon component supplied by the paper to the sidestream smoke particle phase is worthy of note (10.9% instead of the calculated 4.3%).

3. Carbon Monoxide, Carbon Dioxide, and Carbonyl Sulfide

On the basis of nonfilter, 85-mm cigarettes of Burley, Virginia, and Oriental tobaccos and the Kentucky Reference Cigarette 1R1, Johnson et al. found the SS/MS ratios for carbon monoxide and carbon dioxide shown in the following table (Table 8) [55].

Table 8.

Browne et al. [8] also studied the effect of filter ventilation on the amounts of carbon monoxide and carbon dioxide occurring in the mainstream and sidestream smoke. The data published by them are presented in Table 9.

Table 9.

The ratios found for the nonventilated cigarettes are in good agreement with the values published by Johnson for the Kentucky Reference Cigarette 1R1 [55].

The carbon monoxide in the sidestream smoke increases at only half the rate with increasing degree of ventilation as does the carbon dioxide (CO: +17.14%; CO_2: 35.4%; reference points: degree of ventilation, 0% and 100%, i.e., "free burn"). From these findings and from the CO_2/CO ratios for mainstream and sidestream smoke, the authors conclude that the combustion of the tobacco in cigarettes is more complete during the pauses between puffs than during the puff.

They thus confirm the suspicion of Harlan and Moseley from 1955 [36] and the data of Johnson [55] and Wakeham [132].

Baker, however, is of the opinion that the higher CO_2/CO ratio in the sidestream smoke is not primarily the result of more complete combustion at the surface of the glowing cone [4], because the ratio of the carbon oxides formed by combustion is only slightly greater in the sidestream smoke than in the mainstream smoke.

This is also expressed in the studies by Johnson's group on the incorporation at atmospheric oxygen into the various components of cigarette smoke [58]*.

Baker assumes that the reduction of carbon dioxide to carbon monoxide on the hot carbon of the glowing cone occurs to a lesser extent in the sidestream smoke than in the mainstream smoke. He justifies this view by the fact that the gases which diffuse from the glowing cone into the sidestream smoke reside for a shorter period in the high-temperature region than those which are drawn through by the puff into the mainstream smoke.

Yoshida et al. also reported in 1979 at the 33rd Tobacco Chemists Research Conference in Lexington, Kentucky, on the effect of filter ventilation on the carbon monoxide content in the mainstream and sidestream smoke [142]. The carbon monoxide content in the mainstream smoke is reduced by filter ventilation, whereas that of the sidestream smoke remains unaffected. But if the tobacco fill weight of the cigarette is increased, the carbon monoxide content of the sidestream

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*According to Johnson et al. [58], between 52 and 61% atmospheric oxygen is incorporated into the CO and CO_2 of the mainstream and sidestream smoke (oxygen component in CO, 57%; oxygen component in CO_2, 73%). Furthermore, it must also be considered that both carbon dioxide and carbon monoxide can also be formed by the thermal decomposition of tobacco components in addition to formation by combustion [18, 19]. At the present time, the available data do not make it possible to make a safe statement as to the relative amount of carbon monoxide which is formed by way of the reduction of carbon dioxide [4].

smoke increases linearly with the weight increase, whereas it remains unchanged in the mainstream smoke.

In his closed 25-m^3 chamber, Hoegg found 69.8 ppm of CO after the smoking of 24 cigarettes (Kentucky Reference Cigarette 1R1) [40]. This corresponds to 75.7 ml of carbon monoxide in the sidestream smoke of the tested cigarette, whereas he found only 16.0 ml in the mainstream smoke. The resulting SS/MS ratio of 4.7 is almost twice as high as that given by Johnson for the same cigarette [55].

Several years before Hoegg, Scasselatti-Sforozolini and Sabino gave 5.89 for nonfilter and 5.47 for filter cigarettes as the SS/MS ratio for carbon monoxide [110]. These authors carried out their determination with Dräger tubes. The accuracy of their data is thus somewhat limited.

Bridge and Corn obtained a value on a similar order of magnitude [7]. They used a "reverse smoker" to smoke 85-mm, nonfilter U.S.-blend cigarettes, from which either the mainstream smoke or the sidestream smoke could be rinsed into an inhalation chamber with a volume of 324 dm^3 with defined air circulation. After three cigarettes were smoked, 22 ppm CO were found (burning time, nine minutes) in the collected secondary smoke. From these data, the authors calculated a SS/MS ratio for CO of 4.6 after taking into account the air exchange in the chamber and the difference in the average burning times of the cigarettes. Their article does not provide any data, however, which would make it possible to compare the "reverse smoker" with the standard analytical smoking method. It is therefore difficult to evaluate whether and to what extent the measurement values given depend on the smoking method chosen.

Further data on carbon monoxide in sidestream smoke have been presented by Jermini et al. [53]. They machine-smoked 100-mm long American-blend filter

cigarettes (filter length, 20 mm) under standard conditions to a butt length of 33 mm in a 30-m^3 airtight chamber. Immediately after the smoking, they obtained a linear relationship between the carbon monoxide content of the room air and the number of cigarettes smoked. After 20 cigarettes were smoked, 53 ppm of CO were found in the room air. This results in a CO content in the sidestream smoke of 99 mg.

The CO values found by Jermini confirm the data given by Harke, who smoked 30 cigarettes in a 38.2-m^3 unventilated room; at the completion of the smoking process, a carbon monoxide concentration of 64 ppm was found [35]. Unfortunately, neither Jermini's study nor Harke's gives the carbon monoxide content of the mainstream smoke of the test cigarette, which means that it is impossible to calculate the CO ratio.

Kampstrup, Hugod, and Larsen determined the carbonyl sulfide content in the mainstream and sidestream smoke of cigarettes by means of gas chromatography (EC detector) [61]. The qualitative verification of the values took place with the combination of gas chromatography and mass spectrometry.

Carbonyl sulfide had already been detected in cigarette smoke by several authors [46, 91, 98]. The values found by Kamstrup et al. are summarized in Table 10. In the gas phase of commercial cigarettes, the authors found between 25 and 30 vol.-ppm of COS (18-21 µg/cigarette); in the gas phase of experimental cigarettes, they found 25-60 vol.-ppm (18-42 µg/cigarette). In the sidestream smoke, they measured between 2 and 4 vol.-ppm carbonyl sulfide. The mainstream smoke values are on the same order of magnitude as those found by Phillipe et al. [98] and by Horton and Guerin [46], but they are lower by a power of ten than those given by Osborne [91]. A SS/MS ratio of 0.03-0.13 is found from the values published by the Kamstrup's group.

Table 10.

Kamstrup et al. removed 200 µl of smoke from the sixth puff by means of a gas-tight syringe for the determination of the carbonyl sulfide in the mainstream smoke. This sample was then analyzed by gas chromatography. The values determined in this way indicate the content in the mainstream smoke under the assumption that the COS concentration is constant over all puffs. For the determination in the sidestream smoke, 20 cigarettes were allowed to burn down by themselves after being stood up vertically under a glass bell. The glass bell was equipped with a chimney-like tube for the removal of the sidestream smoke, from which the samples were then taken for analysis. Because of the necessarily increased temperature under the bell, this method for collecting smoke does not correspond at all to the analytical smoking as specified in DIN 10,240 [26] or ISO 3,308 [49].

In addition, Souza et al. point out the possible decomposition of sulfur-containing gases on uncoated glass surfaces [123]. These decompositions could occur under the conditions prevailing inside the bell. The COS values given by Kamstrup are therefore in our opinion to be considered as orientational. This is especially true for the data pertaining to the sidestream smoke.

4. Water

Studies on the water content in sidestream smoke have been published by Neurath et al. [85], Seehofer et al. [117], and Browne et al. [8].

According to Neurath, the SS/MS ratio for water is 24; according to Seehofer, 95% of the water formed during the smoking of a cigarette is found in the sidestream smoke. Browne confirms these values. The water content of the sidestream

smoke is only slightly affected by filter ventilation. Almost all the water occurring in the sidestream smoke is in the gas phase [8, 117] (ratios in the mainstream smoke according to Seehofer et al.: 37.12% in the particle phase and 62.88% in the gas phase [117]).

With the help of a synthetic atmosphere (N_2-$^{18}O_2$-$^{16}O_2$ with 49 atom-% ^{18}O), Johnson et al. were able to determine that atmospheric oxygen is incorporated to a much greater extent into sidestream-smoke water during the smoking of cigarettes than into mainstream smoke. They assume that some of the sidestream-smoke water is formed by the oxidation of the hydrogen formed in the glowing cone. It has been found from pyrolysis studies that hydrogen can be formed extremely rapidly by thermal decomposition in the temperature range of 450-900°C [3]. About one-third of the hydrogen thus formed can be oxidized in the presence of oxygen into water.

According to Baker [4], the hydrogen is formed inside the oxygen-poor region of the glowing cone. The hydrogen component which diffuses out of the ember near the carbonaceous zone of the paper comes together with oxygen entering at that point. The high temperatures prevailing in this location lead to the formation of water. If the hydrogen is drawn into the mainstream smoke, however, it cools down to below 100°C, before the oxygen diffusing into the cigarette body reaches a level sufficient for oxidation to occur.

In this regard Johnson et al. [58] and Baker [4] established that atmospheric oxygen is usually incorporated preferentially into the compounds emitted with the sidestream smoke.

5. Carbonyl Compounds and Carboxylic Acids

Preliminary data on the quantitative ratios of various carbonyl compounds

between the sidestream and mainstream smoke of nonfilter cigarettes from Burley, Virginia, and Oriental tobaccos and the Kentucky Reference Cigarette 1R1 have been published by Johnson [55]. They are summarized in Table 11.

Table 11.

Additional data on the occurrence of these compounds in the sidestream smoke are given by Jermini et al. [53]. The amounts of the individual compounds in the sidestream smoke listed in Table 12 were determined from the measurement values found in the room air of their climate-controlled chamber after the machine-smoking of cigarettes. The ratios in the table were calculated with the help of the amounts of the corresponding carbonyl compounds found in the mainstream smoke by other authors and are to be considered only orientational.

Table 12.

Johnson et al. find 1,260 µg of acetaldehyde in the sidestream smoke and 919 µg in the mainstream smoke from the Kentucky Reference Cigarette 1R1 [58, 59]. This gives a SS/MS ratio of 1.37.

Within the scope of their studies on the incorporation of atmospheric oxygen into tobacco smoke components, Johnson et al. measured the acetic acid content in the mainstream and sidestream smoke of the Kentucky Reference Cigarette 1R1 [58, 59]. In the particle phase of the sidestream smoke they measured 355 µg per cigarette, and 530 µg per cigarette in the mainstream smoke. This results in a SS/MS ratio of 0.67. For the total acids, however, Harris and Hayens give a SS/MS ratio of 1.0-1.7 (nonfilter cigarette) and 11 for a filter cigarette [37].

According to Johnson, the SS/MS ratio for acetamide in the particle phase of cigarette smoke is 1.40 (SS, 70 µg; MS, 50 µg) [58, 59].

6. Nitrogen

A nitrogen balance for the Kentucky 1R1 Research Cigarette was set up by Hardy and Hobbs. Only the first five puffs were used for the analysis. The results they found are given in Table 13.

Table 13.

Because the butt lengths established in the relevant standards were not observed when the cigarettes were smoked, the data given are not generally valid.

In the scope of their studies on the formation of molecular nitrogen during the smoking of cigarettes, Johnson et al. established that this is almost exclusively emitted in the sidestream smoke [56].

The data published by this group for the nonfilter Kentucky 1R1 cigarette and for the experimental cigarettes made from Burley, Virginia, and Oriental tobaccos are listed in Table 14.

Table 14.

For the Kentucky 1R1 cigarette, 2.7 mg of the molecular nitrogen formed during smoking were detected in the sidestream smoke, whereas less than 10 µg were found in the mainstream smoke. This results in a SS/MS ratio of more than 270.

Johnson's group carried out their tests with cigarettes enriched with ^{15}N--nitrates, which were smoked in a helium-oxygen atmosphere ($He:O_2$ = 80:20). They could thus provide clear proof that a significant component of the nitrogen contained in the tobacco is converted into molecular nitrogen. Both the nitrate anion and the ammoniacal nitrogen from glycine represent the source of the

molecular nitrogen. The point that glycine can also serve as a starting material for the nitrogen in the sidestream smoke was also found by means of cigarettes treated with ^{15}N-glycine. For the N_2 determination in the smoke, the gas phase was separated by gas chromatography and analyzed by mass spectrometry at a low electron impact energy.

The $^{15}N^{15}N/^{14}N^{15}N$ ratio found by the authors is about the same for the molecular nitrogen of the sidestream smoke and also for the nitrogen which was obtained from the SS-ammonia by oxidation with sodium hypobromite for the cigarette treated with ^{15}N-glycine (Table 15). It is therefore assumed by this research group that nitrogen formation occurs by way of ammonia as an intermediate stage [56].

Table 15.

As further proof of this, Johnson et al. indicate that the SS ratio of ammonia to oxygen was about 1.9 for all cigarettes tested with the exception of the Burley type.

Baker [4] assumes that this oxidation could occur after the diffusion of the ammonia from the inner reducing region of the glowing cone by means of the oxygen penetrating into the boundary zones according to the equation:

He points out, however, that data on the kinetics of a reaction such as this under the conditions which prevail at the periphery of the glowing cone [5] are not currently available.

Hardy and Hobbs studied the contribution which the nitrate ion makes to the formation of a series of gas-phase components of the mainstream and sidestream

smoke by means of isotope dilution [34]. The cigarettes used for the tests were loaded with $Na^{15}NO_3$ or $Na^{15}N^{18}O^{16}O_2$. According to these authors, the nitrate makes no contribution to the molecular nitrogen of the sidestream smoke.

7. Hydrocyanic Acid and Nitriles

Preliminary data on the occurrence of hydrocyanic acid and nitriles in sidestream smoke are to be found in an article by Johnson et al. [55]. As can be seen from Table 16, hydrocyanic acid occurs primarily in the mainstream smoke, whereas the acetonitrile occurs in the sidestream smoke. By means of pyrolysis experiments, the authors established that the hydrocyanic acid is formed only at temperatures of over 600°C. It is of interest, furthermore, that the hydrocyanic acid in the mainstream smoke is to be found both in the particle phase and in the gas phase, but in the sidestream smoke it is to be found only in the particle phase. The amount of the two compounds occurring in the smoke shows a definite dependence on the type of tobacco.

Table 16.

Brunnemann et al. determined the hydrocyanic acid content of the mainstream and sidestream smoke of a series of cigarettes and cigars [14]. The results found by this group are summarized in Table 17 (cigarettes) and Table 18 (cigars).

Table 17.

Table 18.

Brunnemann determined the hydrocyanic content by gas chromatography after

conversion to cyanogen chloride. He also studied the extent to which the mainstream smoke value can be falsified by dicyanogen. For the sidestream smoke/mainstream smoke ratio for hydrocyanic acid of the Kentucky Reference Cigarette 1R1, Brunnemann gives 0.28. The value is many times larger than that calculated from Johnson's data [55]. It is also worthy of note that Brunnemann, in contrast to Johnson, was able to detect hydrocyanic acid in the sidestream smoke in the gas phase in addition to finding it in the particle phase.

The data given by Harris and Hayens for the SS/MS hydrocyanic distribution are somewhat higher than those of the other authors [37]. For a filter cigarette, a high ratio of 3.3 is found from the data provided. This suggests that this cigarette was equipped with a filter which had high selectivity for hydrocyanic acid or that the filter was ventilated.

The group around Jermini, Weber, and Grandjean [53] determined the sidestream smoke values for five different nitriles. For this purpose, 100-mm-long American-blend filter cigarettes were smoked in a 272-liter airtight Plexiglass chamber. One cubic meter of air was loaded with the volume concentrations of nitriles per cigarette shown in Table 19; from these figures, the sidestream smoke values for these compounds could then be calculated.

Table 19.

The acetonitrile content of the sidestream smoke according to this study is on the same order as that given by Johnson [49].

The sources of the hydrocyanic acid and nitriles in tobacco smoke were also discussed by Johnson's group. With the help of cigarettes loaded with $^{15}NO_3^+$, they were able to establish that at least some of the hydrocyanic acid and nitriles is formed from the tobacco nitrate [57]. The formation is said to proceed

again over the intermediate stage of ammonia. Amino acids also make a contribution to the hydrocyanic acid present in cigarette smoke [54]. As already indicated, the SS/MS ratio for this compound is very low.

The reason for this could be the high temperatures required for the formation of hydrocyanic acid [55], which are not reached during the pauses between puffs. During a puff, however, the temperature increases to the required level only at the base of the glowing cone, and the hydrocyanic acid formed at this point is carried over into the mainstream smoke [4].

According to Hardy and Hobbs [34], tobacco nitrate makes only a small contribution to the acetonitrile content of the mainstream smoke, whereas a relatively high percentage of the hydrocyanic acid is formed from it. For the sidestream smoke, the two authors conclude from their findings that these two compounds form to only a moderate extent from tobacco nitrate.

8. pH of the Tobacco Smoke

Wenusch was the first to demonstrate (1930) that the mainstream and sidestream smoke from Oriental tobacco cigarettes differ in their pH. The mainstream smoke shows a weakly acidic reaction, whereas the sidestream smoke shows a weakly basic reaction [136].

Brunnemann and Hoffmann [9] determined the pH of the fresh mainstream and sidestream smoke of a series of cigarettes and cigars; the mainstream smoke of each individual puff was analyzed. The procedure used by them was based on a measurement method developed by Sensabaugh and Cundiff [113], in which the native smoke is conducted over a suitable glass electrode.

According to Brunnemann and Hoffmann, the pH of the mainstream smoke of blend cigarettes is between 5.6 and 6.3, and that of the sidestream smoke is

around seven or higher. For cigarettes of the dark type, mainstream smoke values of 6.6-7.4 and sidestream smoke values of around 7.0-8.0 were found. The corresponding values for cigars are: mainstream smoke, 6.5-8.1; sidestream smoke, 7.5--8.5 (small cigars). The pH values of the mainstream and sidestream smoke of cigarettes show a clear dependence on the type of tobacco burned; and in the mainstream smoke, there is a more or less pronounced drop with the number of puffs.

Klus, Begutter, and Ultsch determined the pH of the mainstream and sidestream smoke of filter-ventilated cigarettes as a function of the degree of ventilation [71]. They were able to show with experimental cigarettes that the pH of the mainstream smoke shifts with an increasing degree of ventilation to the alkaline region and thus approaches the value of the sidestream smoke. For the next-to-last puff, the pH of the unventilated cigarette is 6.40; at a degree of ventilation of 15%, a value of 6.46 found; at 25%, 6.61; at 35%, 6.72; and 50%, 6.98; and at 70%, 7.25. The smoke pH of the sidestream smoke was 8.07.

That the mainstream smoke in qualitative terms approaches that of the sidestream smoke as the degree of filter ventilation increases was already discussed by Browne et al. [8].

Klus et al. [71] determined the smoke pH with the help of a modified procedure, which is also based on the method proposed by Sensabaugh and Cundiff [118] and modified by Sloan and Morie [120].

9. Ammonia, Amines, Nitrogen Bases

As early as 1930, Wenusch established that the sidestream smoke of cigarettes shows, in contrast to the mainstream smoke, a weakly alkaline reaction [136]. He explained this difference by the fact that in the sidestream smoke, nicotine and certain nitrogen bases are present in an nonprotonated form.

Other earlier studies on the concentration of ammonia and nitrogen bases in sidestream smoke were carried out by Pyriki [102, 103, 104, 105, 106], Preiss [101], and Müller and Moldenhauer [80].

The first values for ammonia in mainstream and sidestream smoke of cigarettes obtained by modern smoking methods were published by Scasselatti-Sforozolini and Sabino [110]. According to these authors, there are 160 µg of ammonia in the mainstream smoke and 7,400 µg in the sidestream smoke, from which a SS/MS ratio of 46 is obtained.

Williams and Hunt detected 5,781 µg of ammonia in the sidestream smoke and 55 µg in the mainstream smoke (SS/MS = 105) [138].

In his studies, Johnson found the values summarized in Table 20 [55].

Table 20.

Brunnemann and Hoffmann determined the ammonia content of the mainstream and sidestream smoke of cigarettes and cigars by means of gas chromatography [10]. The sidestream smoke of the tested cigarettes contained up to 73 times more ammonia than the mainstream smoke; in the sidestream smoke of a cigar, up to 670 times more was found (Table 21).

Table 21.

For ammonia, Harris and Hayens found SS/MS ratios between 156 and 1,263 as a function of the mixture and makeup of the cigarette [37].

Further data on ammonia in the mainstream and sidestream smoke of cigars have been published by Schmeltz et al. [114]. For small cigars, a SS/MS ratio of 40-47 was found and for a Manila cigar, the value found was 670, whereby 106 mg of ammonia was detected in the sidestream smoke.

Mechanistic considerations on the formation of ammonia during the smoking of tobacco were again carried out by Johnson et al. [57]. According to this group, ammonia forms through the reduction of the nitrate contained in the tobacco and by the pyrolysis of the amino acid glycine. According to Baker, [4], these reactions occur primarily in the central high-temperature zone of the glowing cone, and a few millimeters from the burn line of the paper. This central region, furthermore, is almost completely unaffected by the air entering during the puff. The gaseous ammonia has more of a tendency to diffuse from its formation zone into the sidestream smoke than to be carried over into the mainstream smoke.

In their work with the Kentucky 1R1 cigarette treated with ^{15}N-nitrate, Johnson et al. [57] were able to show that 25% of the nitrogen added in the form of calcium nitrate is converted into ammonia of the sidestream smoke.

Hardy and Hobbs [34] conclude from the data of their measurements of cigarettes treated with ^{15}N-nitrate that the ammonia of the gas phase of the mainstream smoke is not formed from the tobacco nitrate. The percentage of added nitrate contributing to the ammonia of the sidestream smoke is also very small according to Hardy and Hobbs.

Sloan and Morie [120] determined the percentage of nonprotonated ammonia in the mainstream smoke of commercial cigarettes, the Kentucky 1R1 Reference Cigarette, cigars, and experimental cigarettes of Burley, Virginia, and dark tobaccos. For the commercial cigarettes, values between 1 and 4 ng were found for a total ammonia content of 28-44 µg. In the Kentucky 1R1 cigarettes, the values were 6 ng and 59 µg. The mainstream smoke of cigarettes of dark tobacco contained 1.2 µg of free ammonia at a total content of 147 µg; the corresponding values for cigars were 2.4 and 310 µg.

According to Sloan and Morie, the percentage of nonprotonated ammonia in the smoke is linked to the smoke pH [119]. According to one of the calculations carried out by them, free ammonia can occur only at a pH higher than five; at a pH of about 8.5, this component increases to about 20%; over pH 11, almost 100% of the base is in the free form [120].

Necessarily, therefore, most of the ammonia of the mainstream smoke is in the particle phase [10, 119].

If these considerations are transferred to the sidestream smoke, it can be assumed on the basis of the pH data published up to now [9, 71] that in commercial cigarettes the protonated form of the ammonia is dominant in this smoke phase as well. According to Brunnemann and Hoffmann, the pH of the sidestream smoke of cigars is over 7.5 [9]. At this pH, according to the calculations of Sloan and Morie [120], only about 5% of the ammonia is free and thus is present primarily in the gas phase.

But Brunnemann and Hoffmann still think that the irritation phenomena in the mucosa and eyes which many people suffer from in rooms filled with cigar smoke are possibly attributable to the nonprotonated ammonia component in the sidestream smoke.

Data on the occurrence of hydrazine in cigarette smoke are also provided by Brunnemann [12]. In the mainstream smoke of a nonfilter, 84-mm U.S.-blend cigarette there are 32 ng of this compound, and three times that amount in the sidestream smoke.

No data are known concerning the content of lower aliphathic amines in the sidestream smoke. Only Harris and Hayens have given data on the distribution of total bases between the two smoke streams of cigarettes [37]. According to these authors, the bases occur preferentially in the sidestream smoke; the ratio is between 15 and 44.

Patrianakos and Hoffmann [94] have reported on the occurrence of aromatic amines in sidestream smoke. The bases were concentrated for this study by solvent distribution, converted to their pentafluoropropionic acid derivative, and separated by gas chromatography in a packed column. The compounds eluted from the column were indicated by means of ECD (^{63}Ni). The sidestream smoke was again collected by means of a modified Neurath chamber. The values found in the mainstream and sidestream smoke of a nonfilter, 70-mm U.S.-blend cigarette are shown in Table 22. From the data summarized there it can be seen that aromatic amines, and ammonia too, occur preferentially in the sidestream smoke. The SS/MS ratio for this group of compounds is between 21 and 68.

Table 22.

For pyridine and 3-vinylpyridine, Glock and Wright give a SS/MS ratio of 10 and 43, respectively [31].

Johnson et al. give the pyridine ratio for the two smoke streams of cigarettes as 14.6 to 24.0 in favor of the sidestream smoke [55]. A strong dependence on the type of tobacco used is observed (Table 23).

Table 23.

The most comprehensive study of pyridine and pyrazine in sidestream smoke has been published by Brunnemann, Stahnke, and Hoffmann [16]. The mainstream and sidestream smoke were precipitated separately in 0.05 *N* sulfuric acid; the bases were concentrated by liquid-liquid distribution and separated and determined by means of gas chromatography. The sidestream smoke was collected by means of the modified Neurath chamber. In addition to cigarettes, cigars were

also included in this study. The results found by this group are shown in Table 24. As can be seen, the concentration of the pyridine derivatives was 28 times higher than in the mainstream smoke. For the cigars, this ratio shifts even farther to the side of the sidestream smoke.

Table 24.

Cornell et al. reported at the 31st Tobacco Chemists Research Conference on the distribution of ammonia and pyridine bases between the mainstream and sidestream smoke of cigars [22]. The cigars were smoked down in a four-channel smoking machine; mainstream and sidestream smoke were collected simultaneously. The basic smoke components were precipitated by means of a combination of a Cambridge filter and an acid liquid trap. For ammonia, SS/MS ratios of 250-1,000 were found; for pyridine and 3-methylpyridine, 10-20; for 3-ethylpyridine, 5-7; and for 3,4-lutidine plus 3-vinylpyridine, 50-150. For these determinations the smoking was carried out in correspondence with the standard smoking parameters for cigars (ICCSS) (20-ml puff volume; puff time, 1.5 secs; 1 puff per 40 secs).

According to Cornell et al., the sidestream-mainstream smoke ratio for ammonia and pyridine is dependent on the type of cigar and on the smoking parameters chosen. At a puff volume of 35 ml, a puff time of 1.5 secs, and a rate of three puffs per minute, this ratio decreases for ammonia to 52, and the ratio for pyridine decreases to 3.4.

8. Nitrogen Oxides

G. Scassellatti-Sforozolini and A. Sabino have reported the occurrence of 51 µg of nitrogen oxides in sidestream smoke and 14 µg in mainstream smoke [110].

From this a SS/MS ratio of 3.6 results. To what extent the amounts found are nitrogen monoxide or nitrogen dioxide is not indicated by the authors.

In the light of more recent analytical results, these values appear to be somewhat low [62]. Adams et al. [1] from the Naylor Dana Institute for Disease Prevention, New York, determined the nitrogen monoxide content of mainstream and sidestream smoke by means of the modified Neurath chamber. For the sidestream smoke of U.S. cigarettes, 2-3 mg of NO were found per cigarette. The authors state that the NO content of the sidestream smoke is 4-10 times as high as that of the mainstream smoke.

Ghiste and Brunnemann [30] of Philip Morris Europe confirm the data of Adams with a sidestream smoke chamber of the same type. They found, however, that the NO content in the sidestream smoke, in contrast to that in the mainstream smoke, is strongly dependent on the flow rate of the air through the chamber (Table 25).

Table 25.

It was also found that there is no clear relationship between the nitrate content of the tobacco and the NO concentration in the sidestream smoke. This was established by means of cigarettes of Burley tobaccos with different nitrate concentrations. In the mainstream smoke, however, the NO content of the smoke clearly increases with the nitrate content of the tobacco [116].

Jermini et al. [53] supplied confirmation of Adams's findings [1]. After the smoking of 15 100-mm long American-blend filter cigarettes in a 30-m^3 room, they found a NO concentration of about 1 ppm in the room air. This corresponds to about 2.7 mg of NO per cigarette in the sidestream smoke.

It is of interest that no nitrogen dioxide could be detected by this group in the room air [53, 135]. As an explanation for this finding, it is stated that

the nitrogen oxide analyses were carried out immediately after the smoking by means of a chemoluminescence unit. There was therefore very little aging of the smoke, which model experiments have shown to lead to the occurrence of high concentrations of nitrogen dioxide [87].

N_2O is an additional nitrogen compound which is to be found almost exclusively in sidestream smoke [59]. For the mainstream smoke, the literature supplies values of 30-44 µg of N_2O per cigarette. Johnson assumes that this compound is formed by the oxidation of ammonia or its derivatives. The basis of this assumption is the study on the incorporation of atmospheric oxygen into various smoke components. In these studies he was albe to show that in the N_2O the oxygen to be found is primarily atmospheric in origin.

The concentration of nitrogen oxides in the mainstream smoke is essentially linked with nitrate content of the tobacco. This is clearly demonstrated by a large number of publications [34, 57, 116]. For the nitrogen oxides of the sidestream smoke, Hardy and Hobbs [34] found that nitrate added to the tobacco makes only a small contribution to the formation of these compounds. As already mentioned, Ghiste and Brunnemann also found no clear relationship between tobacco nitrate and nitrogen monoxide content in sidestream smoke [30].

9. *N*-Nitrosamines

In 1977 the group around Hoffmann reported for the first time on the occurrence of volatile *N*-nitrosamines in sidestream smoke [13]. For this study, in which the mainstream smoke was also included, the nitrosamine-specific, highly sensitive thermal energy analyzer (TEA) was used. The sidestream smoke was again collected in the modified Neurath chamber. The results found by this research group are given in the following table.

Table 26.

Brunnemann et al. studied the nitrosamine content of German and Swiss commercial cigarettes by means of an experimental set-up similar to that used by Hoffmann's group [17]. A summary of the analytical results is given in Tables 27 and 28.

Table 27.

Table 28.

The data published by Brunnemann [17] are in particular somewhat lower for the sidestream smoke than those worked out by Hoffmann [13]. When the analytical results and ratios given in Tables 26-28 are evaluated, it must be remembered that *N*-nitrosamines are selectively retained by acetate filters used for the production of modern filter cigarettes. Morie [79] and the Hoffmann group had already pointed this out [13, 43]. A discrimination between the sidestream smoke and the mainstream smoke in terms of the content of volatile nitrosamines thus necessarily results in a comparison of the ratios between filter and nonfilter cigarettes.

It must also be kept in mind that the nitrosamines values listed in the table were also collected by means of the modified Neurath chamber described in this review as early as the second chapter. Brunnemann et al. [17] found that in a 20.87-m^3, hermetically sealed room, the amount of dimethylnitrosamine found in the room air after machine-smoking was only 68-87% of the value to be expected according to the results obtained by means of the modified Neurath chamber (Table 29). The authors emphasize, however, that this experiment, too, requires

critical evaluation with respect to the nitrosamine exposure of humans by virtue of passive smoking, because according to Weber, eye irritations are caused after only five cigarettes are smoked in a 30-m^3 room [134].

Table 29.

Sehlik et al. also compared the content of volatile nitrosamines in sidestream smoke as obtained by means of the modified Neurath chamber with the concentrations of this class of compounds caused by smoking in a hermetically sealed 10-m^3 room.

The values given by this group for dimethylnitrosamine in the sidestream smoke of cigarettes as obtained by means of the modified Neurath chamber are also below the data of Hoffmann's group (Table 30).

Table 30.

Stehlik et al. [124] were able to confirm Brunnemann's conclusion that in a closed room, the dimethylnitrosamine concentration in the room air reached after the smoking of cigarettes is about 25% under the values which would be expected according to the results found with a Neurath chamber (Table 31).

They were also able to show that in a closed room, there is a linear relationship between the number of cigarettes smoked and the dimethylnitrosamine content of the room air. This was not found for the pyrrolidinenitrosamine.

The explanation for this could possibly be a difference in sedimentation rates between the two nitrosamines (difference in the vapor pressure and polarity).

Table 31.